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(54) LITHIUM SECONDARY BATTERY

(57)Abstract:
PURPOSE: To use the complex particles of Li2MnO3 and LiMO2 (where, M is at least one element selected from Co and Ni) as an electrode material for a positive electrode.
CONSTITUTION: The activity of LiMO2 having high activity to the decomposition of a solvent for a nonaqueous electrolyte is decreased due to complexation with Li2MnO3. The result evolves less solvent decomposition on the surface of a positive electrode and less degradation in the nonaqueous electrolyte even if charge and discharge is repeated. Thus, a battery has superior charge discharge cycle characteristics.

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CLAIMS

[Claim(s)]
[Claim 1] It sets to a lithium secondary battery equipped with a positive electrode, a negative electrode, and the nonaqueous electrolyte that consists of a solute and a solvent, and said positive electrode is Li2 MnO3. Lithium secondary battery characterized by using as an electrode material a complex particle with LiMO2 (however, at least a kind of element with which M was chosen from Co and nickel).
[Claim 2] Said complex particle is LiMO2. To the interior of a particle, it is Li2 MnO3. Lithium secondary battery according to claim 1 which is the thing which it comes to contain on a particle front face, respectively.
[Claim 3] Said complex particle is LiMO2. Li2 MnO3 Lithium secondary battery according to claim 1 which is the thing which comes to be intermingled in homogeneity in a particle.
[Claim 4] Said complex particle is a lithium secondary battery according to claim 1 whose value of the ratio of the atomic number of Mn to the total atomic number of M and Mn is the thing of 0.005-0.2.
[Claim 5] The lithium secondary battery according to claim 1 to 4 said whose solvent is a mixed solvent of an annular carbonate and un-annular carbonate, or an annular carbonate and an un-annular carbonate.

DETAILED DESCRIPTION

[Detailed Description of the Invention]
[0001]
[Industrial Application] This invention relates to amelioration of the positive electrode aiming at improving in detail the charge-and-discharge cycle property of the lithium secondary battery which uses LiMO2 (at least a kind [However, M Co and nickel]) as positive active material with respect to a lithium secondary battery.
[0002]
[Description of the Prior Art] Since it has an advantage, like the energy density in which high-voltage-izing is possible is high when it selects positive active material suitably in recent years, since a lithium secondary battery does not need to take the decomposition voltage of water into consideration, it is observed as a next-generation rechargeable battery.
[0003] LiCoO2 which ** and shows high potential in a charge condition as positive active material of the lithium secondary battery of a high-voltage mold, LiNiO2, and LiNi0.5 Co 0.5O2 etc. -- the lithium content transition-metals oxide expressed with a general formula LiMO2 (at least a kind [However, M Co and nickel]) is proposed.
[0004] However, since it originates in positive active material having high activity to disassembly of the solvent of nonaqueous electrolyte and disassembly of a solvent takes place on the surface of a positive electrode, there is a problem that a charge-and-discharge cycle property is not good in the lithium secondary battery which used this kind

of positive active material.
[0005] The place which this invention is made so that it may solve this problem, and is made into that purpose is to offer the lithium secondary battery excellent in the charge-and-discharge cycle property that disassembly of a solvent cannot take place easily.
[0006]
[Means for Solving the Problem] For the lithium secondary battery (the "this invention cell" is called below.) concerning this invention for attaining the above-mentioned purpose, it sets to a lithium secondary battery equipped with a positive electrode, a negative electrode, and the nonaqueous electrolyte that consists of a solute and a solvent, and said positive electrode is Li2 MnO3. Let a complex particle with LiMO2 (however, at least a kind of element with which M was chosen from Co and nickel) be an electrode material.
[0007] As the above-mentioned complex particle, it is LiMO2, for example. What contains Li2 MnO3 on a particle front face inside a particle, respectively, and LiMO2 Li2 MnO3 What is intermingled in homogeneity is mentioned into a particle. LiMO2 To the interior of a particle, it is Li2 MnO3. The complex particle contained on a particle front face, respectively is desirable when obtaining a lithium secondary battery with a large discharge capacity.
[0008] Moreover, the thing of 0.005-0.2 has [the complex particle in this invention cell] the desirable value of the ratio of the atomic number of Mn to the total atomic number of M and Mn. When the value of this ratio separates from this range, there is an inclination for a charge-and-discharge cycle property to fall.
[0009] When obtaining the lithium secondary battery excellent in the charge-and-discharge cycle property especially as a solvent of the nonaqueous electrolyte of this invention cell, the mixed solvent of an annular carbonate and un-annular carbonate, or an annular carbonate and an un-annular carbonate is desirable.
[0010] As an annular carbonate, ethylene carbonate, propylene carbonate, butylene carbonate, and vinylene carbonate are illustrated, and dimethyl carbonate, diethyl carbonate, and methylethyl carbonate are illustrated as an un-annular carbonate. Especially in an annular carbonate, ethylene carbonate is desirable.
[0011] As a solute of the nonaqueous electrolyte of this invention cell, they are LiPF6, LiClO4, LiBF4, and LiCF3 SO3. Although illustrated, it is not restricted especially.
[0012] As a negative electrode of this invention cell, what is used as an electrode material is illustrated [lithium / occlusion and the matter which can be emitted or / metal] in a lithium ion. Considering a lithium ion as occlusion and matter which can be emitted, lithium alloys, such as carbon materials, such as a graphite, corks, and an organic substance baking object, and a lithium-aluminium alloy, a lithium-tin alloy, a lithium-lead alloy, are illustrated.
[0013]
[Function] Li2 MnO3 Since the complex particle with LiMO2 (active material) is used as a positive-electrode ingredient, disassembly of the solvent in the front face of a positive electrode stops being able to happen easily, and a charge-and-discharge cycle property improves. This is Li2 MnO3 in a complex particle. LiMO2 which shows high activity to disassembly of a solvent It thinks for reducing activity. Incidentally, it is Li2 MnO3. It does not participate in charge and discharge.
[0014] Especially, it is LiMO2. To the interior of a particle, it is Li2 MnO3. A charge-

and-discharge cycle property not only improving, when the complex particle contained, respectively is used for a particle front face as a positive-electrode ingredient but a reason is LiMO2 although it now is not certain. A utilization factor improves and discharge capacity also increases.

[0015]

[Example] It is possible to change this invention suitably in the range which is not limited to the following example at all and does not change the summary, and to carry out hereafter, although this invention is further explained to a detail based on an example.

[0016] (Example 1)

[Production of a positive electrode] Li2 CO3 CoCO3 After mixing by the atomic ratio 1.2:1.0 of Li:Co, it heat-treats by 850-degreeC for 10 hours, and it is Li1.2 CoO2. It obtained. Subsequently, this Li1.2 CoO2 MnO2 After mixing by the atomic ratio 1.0:0.1 of Co:Mn, it heat-treated by 850-degreeC for 10 hours, and the positive-electrode ingredient was produced.

[0017] When Ar ion etching analyzed this positive-electrode ingredient from a front face to the interior of a particle gradually using X-ray photoelectron spectroscopy, it turned out that Mn exists only in a front face. This fact to this positive-electrode ingredient is LiCoO2. To the interior of a particle, it is Li2MnO3. It checked that it was what consists of a complex particle contained on a particle front face, respectively.

[0018] Subsequently, after mixing the above-mentioned positive-electrode ingredient, the carbon powder as an electric conduction agent, and the fluororesin as a binder by the weight ratio 80:10:10, it cast to the pellet type and the positive electrode was produced.

[0019] [Production of a negative electrode] The metal lithium rolled plate was pierced and the negative electrode was produced.

[0020] [Preparation of nonaqueous electrolyte] It is LiPF6 to ethylene carbonate (EC). One mol /was melted l. and nonaqueous electrolyte was prepared.

[0021] [Assembly of a cell] this invention cell A1 of positive-electrode rule of a flat mold was assembled using a positive electrode, an above-mentioned negative electrode, and above-mentioned nonaqueous electrolyte (cell dimension: the outer diameter of 24.0mm, thickness of 3.0mm). In addition, as a separator, the fine porosity film made from polypropylene was used.

[0022] (Example 2) Li2 CO3 CoCO3 MnO2 After mixing by the atomic ratio 1.2:1.0:0.1 of Li:Co:Mn, it heat-treated by 850-degreeC for 20 hours, and the positive-electrode ingredient was produced.

[0023] When this positive-electrode ingredient was analyzed by the same X-ray photoelectron spectroscopy as the point, it turned out that Mn is distributed over homogeneity ranging from the front face to the interior. This fact to this positive-electrode ingredient is LiCoO2. Li2 MnO3 It checked that it was what consists of a complex particle intermingled in homogeneity into a particle.

[0024] Subsequently, this invention cell A2 was assembled like the example 1 except having used this positive-electrode ingredient.

[0025] (Example 3) Li2 CO3 CoCO3 nickel2 (OH) After mixing by the atomic ratio 1.2:0.5:0.5 of Li:Co:nickel, it heat-treats by 850-degreeC for 10 hours, and it is Li1.2 Co0.5 nickel 0.5O2. It obtained. Subsequently, these Li1.2 Co0.5 nickel0.5 O2 and MnO2 After mixing by the atomic ratio 1.0:0.1 of Co+nickel:Mn, it heat-treated by 850-degreeC for 10 hours, and the positive-electrode ingredient was produced.

[0026] When this positive-electrode ingredient was analyzed by the same X-ray photoelectron spectroscopy as the point, it turned out that Mn exists only in a front face. This fact to this positive-electrode ingredient is LiCo0.5 nickel 0.5O2. To the interior of a particle, it is Li2 MnO3. It checked that it was what consists of a complex particle contained on a particle front face, respectively.
[0027] Subsequently, this invention cell A3 was assembled like the example 1 except having used this positive-electrode ingredient.
[0028] (Example 1 of a comparison) Li2 CO3 CoCO3 After mixing by the atomic ratio 1.0:1.0 of Li:Co, it heat-treats by 850-degreeC for 20 hours, and it is LiCoO2. It obtained. This LiCoO2 The comparison cell B1 was assembled like the example 1 except having used it as a positive-electrode ingredient.
[0029] (Example 2 of a comparison) Li2 CO3 CoCO3 nickel2 (OH) After mixing by the atomic ratio 1.0:0.5:0.5 of Li:Co:nickel, it heat-treats by 850-degreeC for 20 hours, and it is LiCo0.5 nickel 0.5O2. It obtained. This LiCo0.5 nickel 0.5O2 Comparison cell B-2 was assembled like the example 1 except having used it as a positive-electrode ingredient.
[0030] [Charge-and-discharge cycle trial] About this invention cell A1 - A3 and the comparison cell B1, and B-2, after charging to 4.1V by 3mA, the charge-and-discharge cycle trial which makes 1 cycle the process which discharges to 3.0V by 3mA was performed, and the charge-and-discharge cycle property of each cell was investigated. A result is shown in drawing 1 . drawing 1 -- the charge-and-discharge cycle property of each cell -- an axis of ordinate -- discharge capacity (mAh) -- moreover, it is the graph by which the number of cycles (time) was taken and shown on the axis of abscissa. Moreover, each discharge capacity of 1 cycle eye of each cell and a 100 cycle eye is shown in Table 1.
[0031]
[Table 1]

電池	放電容量（mAh）	
	1サイクル目	100 サイクル目
A1	80	76
A2	68	61
A3	80	75
B1	75	26
B2	75	20

[0032] this invention cell A1 - A3 have few falls of the discharge capacity accompanying the repeat of charge and discharge compared with the comparison cell B1 and B-2, and drawing 1 and Table 1 show excelling in the charge-and-discharge cycle property.
[0033] Especially, it is LiMO2. To the interior of a particle, it is Li2 MnO3. In this invention cell A1 and A3 which used the complex particle contained, respectively for the particle front face as a positive-electrode ingredient, it turns out that the discharge capacity in early stages of a charge-and-discharge cycle also increases.
[0034] [The class of solvent of nonaqueous electrolyte and relation of a charge-and-discharge cycle property] 12 sorts of this invention cell A4-A15 from which only a

solvent differs were assembled like the example 1 except having used the various solvents which replace with ethylene carbonate and are shown in Table 2 as a solvent of nonaqueous electrolyte. Subsequently, about each of these cells, the charge-and-discharge cycle trial was performed on the same conditions as the point, and each discharge capacity of 1 cycle eye of each cell and a 100 cycle eye was calculated. A result is shown in Table 2. In addition, the result of this invention cell A1 assembled in the example 1 is also posted and shown in Table 2 from Table 1.

[0035]

[Table 2]

電池	溶媒（混合溶媒の体積比は全て1：1）	放電容量（mAh）	
		1サイクル目	100 サイクル目
A1	EC	80	76
A4	PC	80	70
A5	BC	80	70
A6	DMC	80	74
A7	DEC	80	76
A8	MEC	80	74
A9	EC／DMC	80	74
A10	EC／DEC	80	76
A11	EC／MEC	80	74
A12	THF	75	60
A13	γ－BL	80	63
A14	DME	75	60
A15	EME	75	60

（注）EC：エチレンカーボネート，PC：プロピレンカーボネート，BC：ブチレンカーボネート，DMC：ジメチルカーボネート，DEC：ジエチルカーボネート，MEC：メチルエチルカーボネート，THF：テトラヒドロフラン，γ－BL：γ－ブチロラクトン，DME：1，2－ジメトキシエタン，EME：1，2－エトキシメトキシエタン

[0036] As shown in Table 2, compared with this invention cells A12-A15, this invention cell A1 and especially A4-A11 have a large discharge capacity of a 100 cycle eye, and are extremely excellent in the charge-and-discharge cycle property. This fact shows that it is desirable as a solvent of the nonaqueous electrolyte in this invention to use the mixed solvent of an annular carbonate and un-annular carbonate, or an annular carbonate and an un-annular carbonate.

[0037] [Relation of the Li2 MnO3 content and charge-and-discharge cycle property of a complex particle] By the same approach as an example 1, it is Li2 MnO3 of a complex particle. Nine sorts of positive-electrode ingredients with which contents differ were produced, and the lithium secondary battery was assembled like the example 1 except having carried out each tales-doses use of these positive-electrode ingredients.

Subsequently, about each of these cells, the charge-and-discharge cycle trial was performed on the same conditions as the point, and each discharge capacity of 1 cycle eye of each cell and a 100 cycle eye was calculated. A result is shown in drawing 2 .

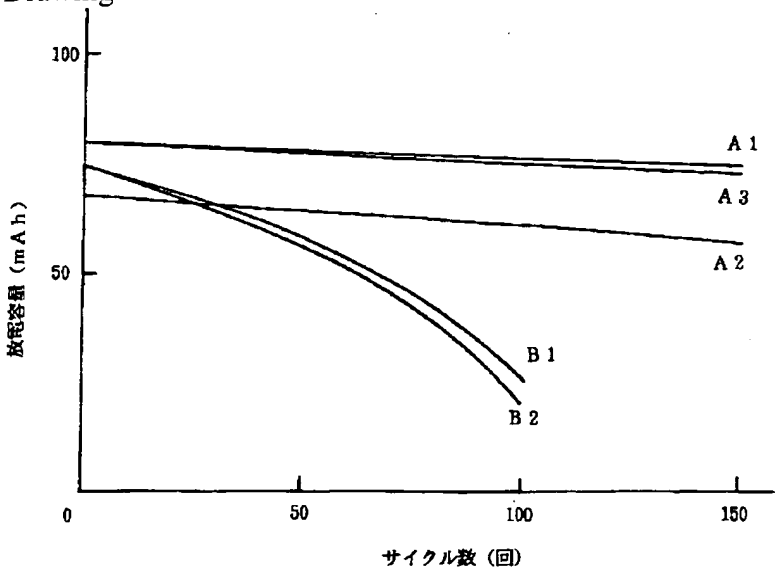
[0038] Drawing 2 is Li2 MnO3 of the complex particle used for each cell. It is the graph by which the value [atomic number [of Mn]/(atomic number of atomic number +Mn of Co)] of the ratio of the atomic number of Mn [as opposed to / in the relation between a content and a charge-and-discharge cycle property / the total atomic number of Co and Mn in a complex particle for the discharge capacity (mAh) of 1 cycle eye or a 100 cycle eye] was taken and shown on the axis of abscissa at the axis of ordinate. Specific Li2 MnO3 whose values of the ratio of the atomic number of Mn to the total atomic number of Co and Mn are 0.005-0.2 in order to obtain the lithium secondary battery excellent in especially the charge-and-discharge cycle property from this drawing It turns out that it is desirable to use the positive-electrode ingredient which consists of a complex particle of a content.

[0039] Although the case where this invention was applied to a flat mold cell was mentioned as the example and the above-mentioned example explained it, especially this invention does not necessarily have a limit in the configuration of a cell, and can be applied to the lithium secondary battery of other various configurations, such as cylindrical and a square shape.

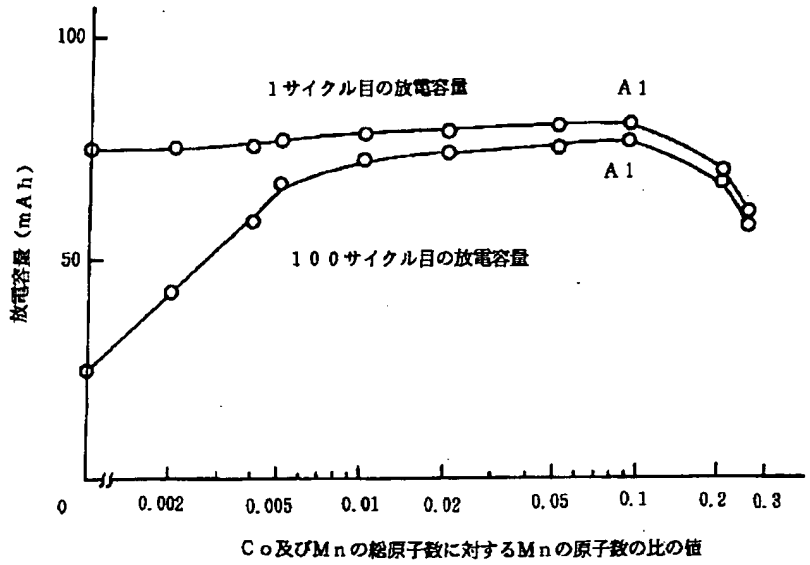
[0040]

[Effect of the Invention] LiMO2 which has high activity to disassembly of the solvent of nonaqueous electrolyte Activity is Li2MnO3. Since it is falling by compound-ization, disassembly of the solvent in the front face of a positive electrode cannot take place easily, and even if it repeats charge and discharge, nonaqueous electrolyte cannot deteriorate easily. For this reason, this invention cell is excellent in a charge-and-discharge cycle property.

Drawing 1



Drawing 2


100
50
0
放電容量（mAh）
1サイクル目の放電容量
A1
A1
100サイクル目の放電容量
0.002
0.005
0.01
0.02
0.05
0.1
0.2
0.3
Co及びMnの総原子数に対するMnの原子数の比の値